Ring-Closing Olefin Metathesis of 3,3′-(D-Glycopyranosylidene)bis(1-propene) Compounds as a Route to Anomeric Spiro Sugars

Guo-Rong Chen,[a] Zhong Bo Fei,[a] Xiao-Ting Huang,[a] Yu-Yuan Xie,[a] Jin-Lou Xu,[a] Joëlle Gola,[b] Michaela Steng,[b] and Jean-Pierre Praly*[b]

Dedicated to Gérard Descotes (University of Lyon, France)[‡]

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New peracetylated 3,3′-(D-glycopyranosylidene)bis(1-propene), prepared from peracetylated anomeric sugar dihalides and allyltributyltin in excess under UV irradiation conditions (AIBN, ca. 35 °C), lent themselves to ring-closing olefin metathesis in the presence of Grubbs′ catalyst (6 mol %) to afford the corresponding peracetylated spiro[1,5-anhydro-D-glycopyranositol-1,4′-cyclopent-1′-enes] (D-*gluco*: 81%, D-*manno*: 89%, D-*galacto*: 72% isolated yield), which could be deacetylated quantitatively. The bis(allylation) reaction (D-*gluco*: 40%, D-*manno*: 34%, D-*galacto*: 24% isolated yield) was in competition with radical-induced rearrangement and elimination reactions. The last process, found to be favored at higher temperature (80 °C), opens an easy route to sugar dienes difficult to prepare otherwise.

Introduction

In a previous paper, we reported on the stereocontrolled synthesis of 3-(β-D-glycopyranosyl)-1-propenes and on access to unknown D-glycopyranosylidenedienes,[1] based on free radical reactions applied to anomeric glycosyl dihalides, such as **1**−**3**. It was of interest to consider treatment of these with an excess of allyltributyltin, as a possible route to 3,3′-(D-glycopyranosylidene)bis(1-propene) derivatives ("*C*,*C*-diallyl glycosides"). Indeed, such compounds had been isolated in trace amounts in the course of our previous investigation.[1] Considering that there are only a few scattered synthetically useful routes, based either on free radical[2] or on ionic[3,4] approaches to *C*,*C*-disubstituted glycopyranosyl compounds, while access to *C*,*C*-spirocyclic glycosides[5,6] often involves carbene intermediates,[7−10] we anticipated that radical-based allylation of these glycosyl dihalides would be a useful and straightforward method applicable to the synthesis of acetylated 3,3′-(D-glycopyranosylidene)bis(1-propenes). Such compounds appeared ideally suited for ring-closing olefin metathesis (RCM)[11−13] to afford new unsaturated spiro sugar derivatives. Indeed, recent interest in olefin metathesis has inspired varied developments in carbohydrate chemistry,[14] in particular concerning *C*-glycosyl compounds,[15] *C*-linked disaccharides,[16] *C*-1 glycals,[17] *C*-glycosylidene compounds,[18] carbasaccharides,[19,20] azasugars,[21] and spiroacetal derivatives.[22] While this work was in progress, a multi-step synthesis of a *gem*-diallyl sugar from a glyconolactone, with the aid of an allyl Grignard reagent, and its successful transformation into the corresponding spirocyclopentene by RCM was reported.[23] We describe here a related approach, applicable to acetylated sugar derivatives.

Results and Discussion

Radical-mediated allylation of the D-*gluco*-chlorobromo sugar **1** was first carried out at ca. 35 °C with an excess of allyltributyltin (6 equiv.) under UV irradiation conditions for ca. 3 h with added AIBN. From several attempts with minor changes in the experimental technique (see Table 1 and Exp. Sect.), it turned out that these conditions produced a mixture of compounds, separable by careful column chromatography and eluted in the following order: **7**, **9**, **12**,[1] then **16**[1] (Scheme 1). Whereas diene **7** was formed in small amounts, as observed previously,[1] the desired compound **9** was obtained in yields not exceeding 40%. Radical-mediated allylation of **1** was repeated as before, except that the temperature was lowered to approximately ca. 0 °C. The diene **7** was formed only in trace amounts at 0 °C, while the (D-glucopyranosylidene)bis(1-propene) **9** was isolated in 24% yield, after repeated chromatographic separations. The acetylated (β-D-glucopyranosyl)-1-propene **12**, containing an unidentified impurity (ca. 2:1 at 0 °C; ca. 3:1 at 35 °C), was also isolated in 10% yield, while a fourth compound (8% yield) was identified as **15**. The reaction was also attempted using a 250-W IR sun lamp instead of a medium-pressure mercury lamp, so that a significantly higher reaction temperature was reached (80 °C). Unexpectedly, the main compound formed at 80 °C in the presence

[a] East China University of Sciences and Technology,
P. O. Box 257, 130 Meilong Road, 200237, Shanghai, P. R. China
[b] Université Claude-Bernard Lyon I, UMR CNRS − Université no. 5622, ESCPE − Lyon, Bât. 308,
43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France
Fax: (internat.) + 33-4/78898914
E-mail: jean-pierre.praly@univ-lyon1.fr
[‡] For his pioneering work in synthetic applications of free-radical reactions and metathesis in carbohydrate chemistry

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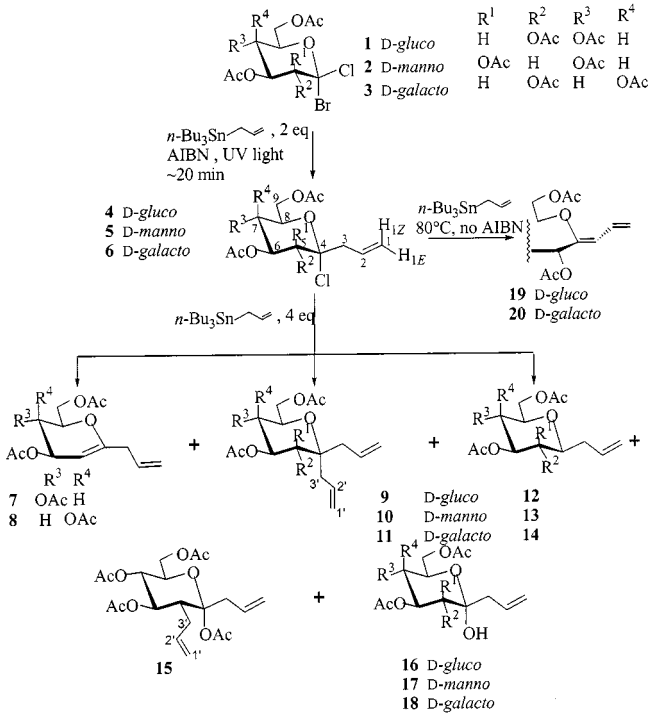
Table 1. Allylation of D-glucopyranosyl halides **1** and **4**: product distribution under various reaction conditions

Entry	Substrate	Conditions[a]			Products yields (%)[b]					
		T [°C]	Bu_3Sn(allyl)[c]	AIBN[d]	**7**	**9**	**12**	**15**	**16**	**19**
1	**1**	ca. 0	2 + 4	+	trace	24	10	8	–	–
2	**1**	ca. 35	2 + 4	+	6	40	12	–	2	–
3	**1**	ca. 35	4 + 2	+	15	24	17	–	19	–
4	**1**	ca. 35	6	+	5	37	11	–	14	–
5	**1**	ca. 80	2 + 3	+	64	10	7	–	–	–
6	**4**	ca. 80	4	+	80	–	–	–	–	–
7	**4**	ca. 80	4	–	–	–	–	–	–	63
8	**4**	ca. 80	1	+	–	–	–	–	–	60

[a] The reaction flask was exposed either to unfiltered UV light (reactions performed at ca. 0 °C and ca. 35 °C) or to visible light from a sunlamp (reactions performed at ca. 80 °C), as described in more detail in the Exp. Sect. – [b] Isolated yields. – [c] Allyltri-*n*-butyltin was added either all at once or portionwise, as indicated (in equiv. amounts). – [d] AIBN was either used in catalytic amounts (+) or omitted (–).

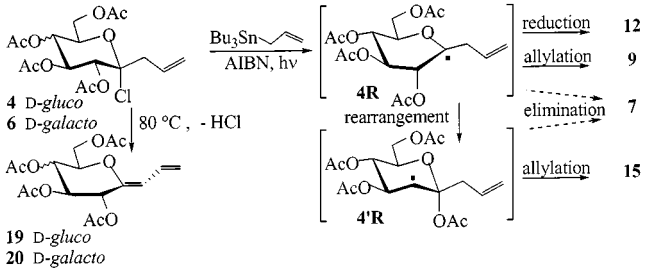
of AIBN was the diene **7**, isolated in 64% yield, while **9** was present in small amounts. As seen from Table 1, use of pure **4** instead of **1** produced **7** in an enhanced yield (80%). Interestingly, when **4** was treated at 80 °C under modified conditions (allyltributyltin/4 equiv., no AIBN; allyltributyltin/1 equiv., catalytic AIBN), the known conjugated glucosylidenediene **19**[1] was formed as the main product (ca. 60% yield). A similar observation was made in the D-*galacto* series, in which the D-*galacto*-configured analog[1] **20** (73% yield) could be obtained from **6** in the absence of AIBN. These trials showed that competing pathways cannot be avoided by changes in the reaction temperature. Bis(allylation) of **2** and **3** was therefore carried out under photolytic conditions at ca. 35 °C and, as in the D-*gluco* series, several compounds were observed: **10**, **13**, and **17** (D-*manno*: 34, 1, and 11% isolated yields respectively); **8**[1] and **11** (D-*galacto*: 7 and 24% isolated yields, respectively; other minor components such as **14** and **18**[1] were not isolated). TLC in each case showed significant amounts of unidentified polar products visible as tails.

While radical-based reduction of the intermediate chlorides **4**–**6** and their hydroxylation (due either to hydrolysis caused by moisture or to reaction of encumbered sugar-derived radicals with remaining molecular oxygen[24]) can explain the occurrence of such products as 3-(β-D-glycopyranosyl)-1-propene **12**–**14** and non-4-ulopyranose derivatives **16**–**18**,[1] respectively, the formation and structures of **7**, **8**, and **15** deserve some comment. Radical routes to 1,2-unsaturated sugars (glycals),[24a] which might explain the formation of **7** and **8**, have been found to be efficient for substrates possessing two vicinal functional groups susceptible to attack by triorganotin radicals, at C-1 and C-2.[25] A few examples have demonstrated the formation of unsaturated sugar derivatives by radical-mediated reductive 1,2-elimination involving acetoxy[26] and pivaloyloxy[27] groups. In particular, attempted radical reduction and allylation of bromonucleoside derivatives upon treatment either with tributyltin hydride or with allyltributyltin at 80 °C produced unsaturated by-products (< 12% yield) as a result of 1,2-elimination of a bromine atom and a pivaloyloxy group. Such a 1,2-elimination was suppressed when the radical allylation was carried out at room temperature with photochemical initiation.[27] Since migration of the acetoxy group from C-5 to C-4 (see Schemes 1 and 3 for numbering of compounds **4**–**15**, and **21**–**25**) took place under our conditions, as evidenced by the formation of **15**, 1,2-elimination might presumably occur for both intermediate radicals **4R** and **4′R** (Scheme 2) in the presence of tributyltin radicals, efficiently producing **7** upon heating (64% from **1**, 80% from **4**). It is conceivable that photostimulated electron transfer might convert long-lived radical **4R** into the corresponding anion, prone to acetoxy group elimination. Of the tri-*n*-butyltin halides, formed as common by-products in radical reactions, the iodide in particular may participate, as a Lewis acid, in unexpected transformations.[28] Since **4** selectively gives **7** (Table 1) upon heating to 80 °C with allyltri-*n*-butyltin and AIBN, and hence in the absence of tri-*n*-butyltin



Scheme 1

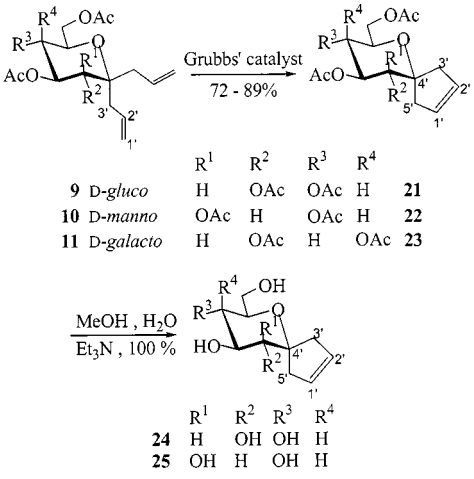
bromide, its participation in the 1,2-elimination process giving **7** from **1** appears improbable. Under conditions which do not favor formation of tributyltin radicals (no AIBN added or quantity of allyltributyltin reduced to 1 equiv., 80 °C), isolation of the conjugated sugar-derived dienes **19** (ca. 60%) and **20** (73%), as major products formed upon attempted allylation of **4** and **6** respectively, shows 1,2-elimination of hydrochloric acid to be the preferred process. Elimination of HCl was shown to occur in **4** upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give **19**,[1] and in a related chlorosugar intermediate produced in boiling benzene solution.[29]



Scheme 2

On the basis of well-established literature data, the rearranged structure of **15** is the result of radical-induced acetoxy group migration, possibly after homolysis of the C4−Cl bond in **4**, followed by allylation of the carbon-centered radical formed at C-5 (**4′R** in Scheme 2). Such rearrangements of glycos-1-yl radicals[30,31] have been exploited as a synthetically useful route[24a] to 2-deoxy sugars,[32] based on a *cis*-2,1-migration of acetoxy,[32,33] chloroacetoxy,[33a] benzoyloxy,[33a] or phosphate groups,[34] preferably in equatorial orientations at C-2. It was shown that equatorially oriented groups at C-2 (D-*gluco*, D-*galacto*, D-*xylo* series) result in α-configured derivatives gaining stabilization through the anomeric effect, whereas β-configured rearranged products are formed in the D-*manno* series at much lower rates because of the weaker stabilization of products: No migration of C-2 acetoxy groups has been observed for D-*manno* configured sugars.[33a,34b] In keeping with these data, no rearranged products were observed when the D-*manno*-configured product **10** was prepared from **2**, which, according to TLC and the isolated product distribution (**10**: 34%; **13**: 1%; **17**: 11%), reacted at ca. 35 °C with a somewhat higher selectivity than **1**. Compound **15** was assigned a D-*gluco* configuration on the basis of the large vicinal coupling constant between 5-H and 6-H ($J_{5,6}$ = 10.7 Hz), showing their *trans*-diaxial orientation. The C-5 epimer of **15** (D-*manno* configuration) was not isolated but it may correspond to the unidentified compound found in admixture with **12** (see above and Exp. Sect.). It was probably formed only in trace amounts, in keeping with the 9:1 and 6:4 diastereoselectivities in favor of the D-*gluco*-branched sugars[35] found for allyltributyltin-mediated allylation of 1,3,4,6-tetra-*O*-acetyl-2-bromo-2-deoxy-β-D-glucopyranose (43% total yield),[35a] and methyl 3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyran-2-yloside radical,[35b] respectively. To the best of our knowledge,[24a] formation of **15** is the first example of acetoxy group migration towards a substituted D-glucopyranos-1-yl radical.

Ring-closing olefin metathesis of compounds **9**−**11** was achieved uneventfully, with Grubbs' catalyst used in catalytic amounts (6 mol %) in dichloromethane as the solvent and under argon. TLC monitoring showed completion of the reactions within ca. 7 h when stirred at room temperature, with formation of a single product. The catalyst in the resulting dark solutions was decomposed in the presence of air[36] prior to product purification by column chromatography. Spiro sugars **21**−**23** were obtained in 81, 89, and 72% yields, respectively, in good agreement with published results.[23] Deacetylation of **21** and **22** was achieved quantitatively in a mixture of $MeOH/H_2O/NEt_3$ (Scheme 3).



	R^1	R^2	R^3	R^4	
9 D-*gluco*	H	OAc	OAc	H	**21**
10 D-*manno*	OAc	H	OAc	H	**22**
11 D-*galacto*	H	OAc	H	OAc	**23**

	R^1	R^2	R^3	R^4
24	H	OH	OH	H
25	OH	H	OH	H

Scheme 3

The ^{13}C NMR resonances of C-3 and C-3′ in **9** were assigned by comparison with literature values reported for 3-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene and the β-anomer **12**.[37] The shieldings observed for C-3′, C-6, and C-8 in the 3,3′-(D-glucopyranosylidene)bis(1-propene) compound **9**, and for the corresponding atoms in 3-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-propene can be explained on the basis of the γ-gauche effect (steric effect),[38] defined as "steric interactions, mostly arising from touching or overlapping of van der Waals radii of closely spaced hydrogens, usually cause a shielding of the carbon atoms attached to these hydrogens". On the basis of the signals assigned to C-3 and C-3′, the four allylic hydrogen atoms in **9** could be assigned by HSQC correlation: The allylic hydrogen atoms on the axially oriented branch were found to be deshielded in comparison to those on the equatorial allyl group, as was also observed for **12** and its α-anomer.[37] Structure assignment for **7**, **8**−**11**, **15**, and **21**−**25** was based on 2D homonuclear and heteronuclear correlations. For **21**, NOESY correlation allowed unambiguous assignments of C-3′and C-5′, the resonances of which can once more be interpreted on the basis of the γ-gauche effect. Assignments proposed for C-3, C-3′, and C-5′ in **10**, **11**, and **22**−**25** follow those determined for **9** and **21**. Homonuclear vicinal

couplings showed that compounds **9**−**11**, **15**, and **21**−**24** existed in $^4C_1$-D chair conformations. It is noteworthy that the compounds observed in the course of this study can be distinguished on TLC plates by characteristic colors visible during the initial stage of charring (ca. 250 °C) after spraying with a 10% H_2SO_4 solution in 1:1 EtOH/water: **4**−**6**: brown; **7**, **8**, **15**: black; **9**−**11**, **21**, **22**: greenish; **12**, **13**: violet; **16**, **17**: beige.

Conclusion

In conclusion, acetylated glycosyl dihalides **1**−**3** have been shown to produce the corresponding 3,3′-(D-glycopyranosylidene)bis(1-propenes) **9**−**11** by free radical mediated allylation in the presence of excess allyltributyltin. The yields achieved when reactions were carried out at ca. 35 °C under UV irradiation conditions (D-*gluco*: 40%, D-*manno*: 34%, D-*galacto*: 24%) compared well to that recently reported for a two-step ionic procedure.[23] Lowering the reaction temperature to ca. 0 °C did not enhance the reaction selectivity, due to competing radical rearrangement, while performing the reaction at 80 °C on heating with an IR sun lamp (AIBN added) mainly produced 3,4,6-tri-*O*-acetyl-1-allyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (**7**) (64% isolated yield). This constitutes a synthetically useful example of 1,2-elimination of a chlorine atom and an acetoxy group favored by heating under radical conditions. The acetylated 3,3′-(D-glycopyranosylidene)bis(1-propenes) **9**−**11** undergo ring-closing metathesis[11] in the presence of Grubbs' catalyst to afford spirocyclopentene derivatives in high yields (D-*gluco*: 81%, D-*manno*: 89%, D-*galacto*: 72%). The obtained spirobicyclic sugars **21** and **22** were deacetylated quantitatively in $MeOH/H_2O/NEt_3$ to afford **24** and **25**.

Experimental Section

General Methods: The NMR spectra were recorded with Bruker spectrometers DRX 300, DRX 500 for solutions in $CDCl_3$, with Me_4Si as the internal reference. − Mass spectra were measured with a FINNIGAN MAT 95 XL spectrometer. − Optical rotations were measured with a Perkin−Elmer 241 polarimeter. − Reactions were monitored by TLC on silica gel 60 F_{254} (E. Merck) plates, developed by exposure to H_2SO_4 (10% in 1:1 EtOH/H_2O) spray followed by charring (ca. 250 °C). Bromine-containing compounds were visible on TLC plates as pink spots, after spraying first with fluorescein (0.1% in ethanol), then with 1:1 H_2O_2 (30% in water)/acetic acid, and charring (ca. 250 °C). − Column chromatography was performed using Geduran Si 60 silica gel (E. Merck). Allyltributyltin and (benzylidene)bis(tricyclohexylphosphane)ruthenium (IV) dichloride (Grubbs' catalyst) were purchased from Aldrich and Strem Chemicals, respectively. Solvents were distilled before use; water was distilled twice. Benzene was distilled from CaH_2. Dichloromethane for RCM reactions was distilled from CaH_2 under argon.

3,4,6-Tri-*O*-acetyl-1-allyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (7), 3,3′-(2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosylidene)bis(1-propene) (9), and 4,6,7,9-Tetra-*O*-acetyl-1,2,3,5-tetradeoxy-5-*C*-allyl-α-D-glucopyranos-1-en-4-ulose (15)

Photoinitiated Reaction at ca. 35 °C: 2,3,4,6-Tetra-*O*-acetyl-1-bromo-β-D-glucopyranosyl chloride (**1**)[39] (222.5 mg, 0.5 mmol), allyltri-*n*-butyltin (330 mg, 1 mmol, 2 equiv.) and a catalytic amount of AIBN were dissolved in dry, deoxygenated benzene (5 mL). The mixture was poured into a stoppered tube made of quartz and argon was introduced. Irradiation with UV light (medium-pressure mercury lamp, Hanovia, 450 W, no filter) was applied for 20 min whereupon the substrate was converted into the chloroallyl intermediate **4**.[1] After addition of another portion of allyltri-*n*-butyltin (660 mg, 2 mmol, 4 equiv.) and AIBN (catalytic), irradiation was continued for 2 h 20 min. TLC monitoring showed the complete conversion of **4** (R_f = 0.48, ethyl acetate/petroleum ether, 1:2). The reaction mixture was stirred overnight in the presence of potassium fluoride (2.3 g), dissolved in water/acetonitrile (2:9, 11 mL), after which the white solids were filtered off and rinsed. After concentration of the organic phase under vacuum, the residue was applied to a column of silica gel and eluted with ethyl acetate/petroleum ether, 1:3, to afford fractions corresponding to **7** (10 mg, 6% yield), **9** (84 mg, 40% yield), **12**[1,37] (24 mg, ca. 12% yield), and **16**[1] (4 mg, 2% yield). Contamination of **12** by an unidentified impurity (ratio: ca. 75:25) was detected by ^1H NMR. Several other minor polar compounds following **12** and **16** (R_f = 0.38, and 0.14, respectively, ethyl acetate/petroleum ether, 1:2) were not isolated. − Two additional syntheses (A and B) of **9** were attempted. They differed in the amount of allyltri-*n*-butyltin (indicated in equiv.) added first (*a*) and after (*b*) conversion of **1** to the chloroallyl intermediate **4** and in the irradiation time: A: (*a*) 4 equiv., 20 min; (*b*) 2 equiv., 6 h; B: (*a*) 6 equiv., 2 h 50 min. The quantities/yields recorded for experiments A and B, respectively, are as follows: **7**: 24 mg, 15%; 8 mg, 5%; **9**: 50 mg, 24%, 76 mg, 37%; **12**: 31 mg, 17%; 21 mg, 11%: **16**: 39 mg, 19%; 27 mg, 14%.

Photoinitiated Reaction at ca. 0 °C: Other experiments conducted with **1** as previously described, but at lower temperature (ca. 0 °C) mainly produced **9**, **12**, and the rearranged product **15** (see Table 1). To maintain the temperature of the reaction medium near 0 °C, we used different devices, in particular a Dewar flask fitted at the bottom with a double envelope quartz tube in which the quartz tube containing the reaction mixture could be fitted (with a distance to the mercury lamp of about 5 cm). The flask was filled with ice/water, to which crushed ice was added occasionally. In other experiments, the quartz tube containing the reagents was placed near the mercury lamp, which was immersed in a ice-cooled water bath. The reaction time was found to be longer when using the Dewar flask (16 h, 4 h, respectively, depending on the applied conditions), due to the lower temperature and increased distance between the tube and the lamp. TLC (petroleum ether/diethyl ether, 1:2) clearly showed the conversion of **4** (R_f = 0.47) mainly into **9**, **12**, and **15**, which were somewhat less mobile (R_f = 0.44, 0.41, 0.44, respectively). With this solvent mixture, **9** and **15**, having the same mobility, could not be separated. Efficient chromatographic separation was achieved with petroleum ether/dichloromethane/diethyl ether, 2:1.5:0.5, in which **9**, **12**, and **15** have R_f values of 0.37, 0.31, 0.27, respectively, after two consecutive elutions of the TLC plates.

Reactions Carried out by Heating to 80 °C with a Sunlamp. − a): Sugar dihalide **1**[39] (200 mg, 0.45 mmol), allyltributyltin (300 mg, 0.9 mmol, 2 equiv.) and a catalytic amount of AIBN were dissolved in dry, deoxygenated benzene (4 mL). The mixture was kept under argon and was irradiated with a 250-W heat lamp for 2 h, until the substrate had been converted into **4** (R_f = 0.45 petroleum ether/diethyl ether, 1:1). Another portion of allyltributyltin (450 mg,

1.35 mmol, 3 equiv.) and a catalytic amount of AIBN were then added to the reaction mixture, which was irradiated for 2 h, until TLC monitoring showed the complete conversion of **4**. Removal of the organotin was achieved as before, and, after concentration of the organic phase under vacuum, the syrup was applied to a column of silica gel and eluted with petroleum ether/diethyl ether, 1:1 to afford **7** (90 mg, 64% yield), **9** (18 mg, 10% yield), and **12** (12 mg, 7% yield). − **b):** When pure chloride **4** (0.2 g, 0.45 mmol) was boiled in benzene (250-W sunlamp, catalytic amount of AIBN, argon) in the presence of allyltributyltin (4 equiv.), diene **7** was isolated in 80% yield. − **c):** Heating **4** for 4:5 h as before [conditions (*b*)] but with no added AIBN produced conjugated diene **19**[1] (63% isolated yield). − **d):** Diene **19** was obtained in 60% yield from **4** on treatment with allyltributyltin (1 equiv.) and AIBN.

Compound 7: Colorless oil, R_f = 0.52 (ethyl acetate/petroleum ether, 1:2). − $[\alpha]_D^{25}$ = +3 (*c* = 0.8, $CHCl_3$). − IR (NaCl, film): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1645, 1675 cm^{-1} (C=C). − ^1H NMR (200.1 MHz, $CDCl_3$): δ = 5.80 (ddt, 1 H, $J_{2,1(Z)}$ = 17.0 Hz, $J_{2,1(E)}$ = 10.2 Hz, $J_{2,3a}$ = $J_{2,3b}$ = 6.7 Hz, 2-H), 5.30 (t, 1 H, $J_{6,7}$ = 3.5 Hz, 6-H), ca. 5.15 (t, 1 H, $J_{7,8}$ = 5.3 Hz, 7-H), 5.0−5.2 [m, 2 H, 1-H(*E*), 1-H(*Z*)], 4.68 (d, 1 H, $J_{5,6}$ = 3.4 Hz, 5-H), 4.42 (dd, 1 H, $J_{9a,9b}$ = 11.6 Hz, 9-Ha), 4.27 (dt, 1 H, $J_{8,9a}$ = 5.6 Hz, $J_{8,9b}$ = 3.1 Hz, 8-H), 4.16 (dd, 1 H, 9-Hb), 2.83 (d, 2 H, 3-Ha, 3-Hb), 2.09, 2.07, 2.04 (3 s, 9 H, acetyl). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 156.2 (C-4), 133.2 (C-2), 118.1 (C-1), 94.9 (C-5), 74.5 (C-8), 68.5 (C-6), 67.6 (C-7), 61.8 (C-9), 38.1 (C-3), 171.0, 170.9, 170.1 (C=O), 21.5, 21.2, 21.1 (acetyl). − $C_{15}H_{20}O_7$ (312.32): calcd. C 57.69, H 6.45, O 35.86; found C 58.08, H 6.80.

Compound 9: Colorless oil, R_f = 0.44 (ethyl acetate/petroleum ether, 1:2). − $[\alpha]_D^{25}$ = +62 (*c* = 1.1, $CHCl_3$). − IR (NaCl, film): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1645 cm^{-1} (C=C). − ^1H NMR (200.1 MHz, $CDCl_3$): δ = 5.76 (m, 2 H, 2-H, 2′-H), 5.34 (t, 1 H, $J_{5,6}$ = 9.8, $J_{6,7}$ = 9.6 Hz, 6-H), 5.12 (d, 1 H, 5-H), 5.08−5.14 [m, 4 H, 1-H(*E*), 1-H(*Z*), 1′-H(*E*), 1′-H(*Z*)], 4.99 (t, 1 H, $J_{7,8}$ = 10.1 Hz, 7-H), 4.12 (d, 2 H, 9-Ha, 9-Hb), 3.84 (dt, 1 H, $J_{8,9a}$ = $J_{8,9b}$ = 3.8, $J_{8,7}$ = 10.1 Hz, 8-H), 2.79 (ddt, 1 H, $J_{3'a,1'(E)}$ = $J_{3'a,1'(Z)}$ ≈ 1 Hz, $J_{3'a,2'}$ = 6.3 Hz, $J_{3'a,3'b}$ = 15.7 Hz, 3′-Ha), 2.44 (ddt, 1 H, $J_{3a,1(E)}$ = $J_{3a,1(Z)}$ ≈ 1 Hz, $J_{3a,2}$ = 6.3 Hz, $J_{3a,3b}$ = 14.6 Hz, 3-Ha), 2.37 (ddt, 1 H, $J_{3'b,1'(E)}$ = $J_{3'b,1'(Z)}$ ≈ 1 Hz, $J_{3'b,2'}$ = 7.5 Hz, 3′-Hb), 2.11 (ddd, 1 H, $J_{3b,1}$ ≈ 1 Hz, $J_{3b,2}$ ≈ 7.5 Hz, 3-Hb), 2.08, 2.03, 2.01, 1.98 (4 s, 12 H, acetyl). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 131.7, 131.0 (C-2, C-2′), 119.3, 119.2 (C-1, C-1′), 72.4 (C-6), 72.1 (C-5), 69.3, 69.1 (C-7, C-8), 62.7 (C-9), 40.9 (C-3), 34.0 (C-3′), 170.7, 170.5, 169.5, 169.1 (C=O), 20.8, 20.8, 20.7, 20.6 (acetyl). The C-4 signal, which was hidden by the $CDCl_3$ resonances at 50 MHz, was visible at δ = 77.8 at 75.47 MHz. −MS (CI, NH_3): *m*/*z* = 413 $[M + 1]^+$, 430 $[M + 18]^+$. − $C_{20}H_{28}O_9$ (412.44): calcd. C 58.24, H 6.84, O 34.91; found C 57.85, H 7.12.

Compound 15: Colorless oil. − $[\alpha]_D^{25}$ = +65 (*c* = 0.5, $CHCl_3$). − ^1H NMR (500.1 MHz, $CDCl_3$): δ = 5.73 (m, 2 H, 2-H, 2′-H), 5.30 (dd, 1 H, $J_{6,7}$ = 9.3, $J_{5,6}$ = 10.7 Hz, 6-H), 5.18 [m, 2 H, 1-H(*E*), 1-H(*Z*)], 4.99 (dd, 1 H, $J_{7,8}$ = 10.3 Hz, 7-H), 4.95 [m, 2 H, 1′-H(*E*), 1′-H(*Z*)], 4.27 (dd, 1 H, $J_{8,9a}$ = 4.6 Hz, $J_{9a,9b}$ = 12.3 Hz, 9-Ha), 4.12 (dd, 1 H, $J_{8,9b}$ = 2.3 Hz, 9-Hb), 3.83 (ddd, 1 H, 8-H), 3.58 (ddt, 1 H, $J_{3a,3b}$ = 14.4 Hz, $J_{3a,2}$ = 4.7 Hz, $J_{3a,1(E)}$ = $J_{3a,1(Z)}$ = 2.0 Hz, 3-Ha), 2.61 (dd, 1 H, $J_{3b,2}$ = 9.6 Hz, 3-Hb), 2.42 (dddd, 1 H, $J_{3'a,3'b}$ = 13 Hz, $J_{3'a,2'}$ ≈ 6 Hz, $J_{3'a,1'(E)}$ ≈ 2 Hz, $J_{3'a,5}$ ≈ 3.5 Hz, 3′-Ha), 2.18 (m, 1 H, 3′-Hb), 2.15 (m, 1 H, 5-H), 2.12, 2.10, 2.04, 1.98 (4 s, 12 H, acetyl). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 136.7 (C-2′), 132.4 (C-2), 119.8 (C-1), 115.6 (C-1′), 107.1 (C-4), 73.3 (C-6), 70.2 (C-8), 69.6 (C-7), 62.4 (C-9), 45.3 (C-5), 39.7 (C-3), 32.6 (C-3′), 171.2, 170.9, 170.4, 168.7 (C=O), 22.6, 21.3, 21.2, 21.1 (acetyl). − MS (CI, isobutane): *m*/*z* = 353 $[M - AcO]^+$, 293 $[M - AcO - AcOH]^+$, 233 $[M - 179]^+$.

3,3′-(2,3,4,6-Tetra-*O*-acetyl-D-mannopyranosylidene)bis(1-propene) (10): In a quartz tube (13 mm external diameter), a mixture containing sugar dihalide **2**[39] (158.6 mg, 0.35 mmol), allyltributyltin (0.44 mL, 1.42 mmol, 4 equiv.), and a catalytic amount of AIBN, dissolved in dry, deoxygenated benzene (3.6 mL), was stirred overnight at room temperature under argon. After the mixture had been cooled with ice/water, the tube was mounted near a medium-pressure mercury lamp (ca. 1 cm distance, no filter), and irradiation was continued for 2.5 h under argon. TLC monitoring (ethyl acetate/petroleum ether, 1:2) showed no traces of **2** after 1 h, and almost complete transformation of the chloroallyl intermediate **5** (R_f = 0.24) to give **10** (R_f = 0.26), and trace amounts of **13** (R_f = 0.20). The organotin compounds were removed by filtration of the solids produced on stirring for 1 h with KF (1.07 g) dissolved in acetonitrile/water (5:1, 3.75 mL). The liquid phase was concentrated under vacuum and the residue was dissolved in acetonitrile (5 mL). Washing with hexanes (3 × 5 mL) and concentration of the acetonitrile phase afforded a residue (171 mg), which was applied to a column of silica gel and eluted with ethyl acetate/petroleum ether, 1:3. Compound **10** (50 mg, 0.12 mmol, 34% yield) was obtained first as a clear syrup, followed by **13**[1] (1.3 mg, 0.035 mmol, 1%), and the ulose derivative **17**[1] (15 mg, 0.04 mmol, 11%).

Compound 10: $[\alpha]_D^{22}$ = +18.5 (*c* = 1.1, acetone). − ^1H NMR (300.1 MHz, $CDCl_3$): δ = 5.75 (dddd, 1 H, $J_{2,1(Z)}$ = 17.6 Hz, $J_{2,1(E)}$ = 9.6 Hz, $J_{2,3a}$ = 5.9 Hz, $J_{2,3b}$ = 7.9 Hz, 2-H), 5.61 (ddt, 1 H, $J_{2',1'(Z)}$ = 17 Hz, $J_{2',1'(E)}$ = 10.0 Hz, $J_{2',3'a}$ = 7.4 Hz, $J_{2',3'b}$ = 7.9 Hz, 2′-H), 5.35 (dd, 1 H, $J_{5,6}$ = 3.3, $J_{6,7}$ = 10.0 Hz, 6-H), 5.25−5.20 [dm, 1 H, $J_{1(E),3a}$ ≈ 1.3 Hz, 1-H(*E*)], 5.25−5.20 [dm, 1 H, $J_{1(Z),3a}$ ≈ 1.3 Hz, 1-H(*Z*)], 5.22 (t, 1 H, $J_{7,8}$ = 10.0 Hz, 7-H), 5.21 (d, 1 H, 5-H), 5.11 [dm, 1 H, $J_{1'(E),1'(Z)}$ ≈ 1.3 Hz, $J_{1'(E),3'a}$ ≈ 1.3 Hz, 1′-H(*E*)], 5.06 [dm, 1 H, $J_{1'(Z),1'(E)}$ ≈ 1.3 Hz, $J_{1'(Z),3'a}$ ≈ 1.3 Hz, 1′-H(*Z*)], 4.19 (dd, 1 H, $J_{9a,9b}$ = 12.0 Hz, $J_{8,9a}$ = 5.7 Hz, 9-Ha), 4.13 (dd, 1 H, $J_{8,9b}$ = 2.8 Hz, 9-Hb), 3.89 (ddd, 1 H, 8-H), 2.66 (ddm, 1 H, $J_{3a,3b}$ = 15 Hz, 3-Ha), 2.40 (ddm, 1 H, 3-Hb), 2.40 (ddm, 1 H, $J_{3'a,3'b}$ = 14 Hz, 3′-Ha), 2.30 (ddm, 1 H, 3′-Hb), 2.17, 2.10, 2.06, 1.97 (4 s, 12 H, acetyl). Proton resonances for the two allyl groups have been assigned tentatively, based on the chemical shift values found for **9**, **13**,[1] and the α-anomer of **13**.[40] − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 131.7, 130.4 (C-2, C-2′), 119.6, 119.4 (C-1, C-1′), 78.4 (C-4), 70.7, 70.2, 70.0, 66.5 (C-5, C-6, C-7, C-8), 63.4 (C-9), 38.5, 34.1 (C-3, C-3′), 170.7, 170.3, 170.2, 169.8 (C=O), 20.8, 20.8, 20.7, 20.6 (acetyl). − MS (CI, NH_3): *m*/*z* = 430 $[M + 18]^+$, 413 $[M + 1]^+$. − $C_{20}H_{28}O_9$ (412.44): calcd. C 58.24, H 6.84, O 34.91; found C 58.44, H 6.92, O 34.62.

3,4,6-Tri-*O*-acetyl-1-allyl-1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (8) and 3,3′-(2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosylidene)bis(1-propene) (11): 2,3,4,6-Tetra-*O*-acetyl-1-bromo-β-D-galactopyranosyl chloride (**3**)[39] (183.8 mg, 0.41 mmol), allyltri-*n*-butyltin (0.25 mL, 0.84 mmol, 2 equiv.) and a catalytic amount of AIBN were dissolved in dry, deoxygenated benzene (4 mL). The mixture was poured into a stoppered tube made of quartz (13 mm diameter) and argon was introduced. Irradiation with UV light (medium-pressure mercury lamp, Hanovia, 450 W, no filter) was applied for 25 min, after which the substrate had been converted into the chloroallyl intermediate **6**. After addition of another portion of allyltri-*n*-butyltin (0.5 mL, 1.68 mmol, 4 equiv.) and AIBN (catalytic), irradiation was continued for 2 h 50 min. TLC monitoring showed the complete conversion of **6**, to give a mixture containing at least 7 products. The reaction mixture was stirred overnight in the presence of potassium fluoride (1.84 g), dissolved in 2:9 water/aceto-

nitrile (8 mL), after which the white solids were filtered off and rinsed. After concentration of the organic phase under vacuum, the residue was dissolved in acetonitrile (15 mL), which was then washed with hexane (3 × 15 mL). The acetonitrile phase was concentrated under vacuum, and the residue was applied to a column of silica gel and eluted with a 1:1 diethyl ether/petroleum ether mixture. Two fractions were collected. The first one (R_f = 0.56, diethyl ether/petroleum ether, 1:1, two successive elutions) was identified as 3,4,6-tri-*O*-acetyl-1-allyl-1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (**8**) (8.7 mg, 7% yield), obtained as a colorless oil. The second fraction (R_f = 0.44, diethyl ether/petroleum ether, 1:1, two successive elutions) was a mixture containing two compounds (50 mg, ratio ca. 8:1). They were separated by chromatography with a column of silica gel and eluted with petroleum ether/dichloromethane/diethyl ether, 2:1.5:0.5. The main compound was identified as the "*C*,*C*-diallyl D-galactoside" **11** (40.6 mg, 24%) with R_f = 0.45, after two successive elutions of the same plate with petroleum ether/dichloromethane/diethyl ether, 2:1.5:0.5. The minor impure fraction (6 mg) which was more polar and the other compounds were not identified. Treatment of **6** as for **4** under conditions (*c*) (see above, 2 h heating to 80 °C) produced the D-*galacto* analog[1] **20** in 73% isolated yield.

Compound 8: Colorless oil. − R_f = 0.56 (diethyl ether/petroleum ether, 1:1, after two successive elutions). − $[\alpha]_D^{22}$ = +2.3 (*c* = 0.5, acetone). − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 5.84 (ddt, 1 H, $J_{1(E),2}$ = 10.1 Hz, $J_{1(Z),2}$ = 16.8 Hz, $J_{2,3a}$ = 6.7 Hz, $J_{2,3b}$ = 6.7 Hz, 2-H), 5.54 (m, 1 H, 6-H), 5.41 (dt, 1 H, $J_{6,7}$ = 4.5, $J_{7,8}$ = 1.6 Hz, $J \approx$ 1.2 Hz, 7-H), 5.20−5.09 [m, 2 H, 1-H(*E*), 1-H(*Z*)], 4.56 (m, 1 H, $J_{5,6}$ = 3 Hz, $J_{5,7}$ = 1 Hz, 5-H), 4.31 (m, 2 H, 8-H, 9-Ha), 4.21 (dd, 1 H, $J_{8,9b}$ = 9 Hz, $J_{9a,9b}$ = 15 Hz, 9-Hb), 2.85 (d, 2 H, 3-Ha, 3-Hb), 2.14, 2.10, 2.05, (3 s, 9 H, acetyl). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 155.9 (C-4), 133.3 (C-2), 118.1 (C-1), 94.8 (C-5), 73.3 (C-8), 65.1 (C-6), 64.2 (C-7), 62.1 (C-9), 38.1 (C-3), 171.1, 170.8, 170.6 (C=O), 21.3, 21.2, 21.2 (acetyl). − CIMS (isobutane): *m/z* (%) = 313 (2) $[M + H]^+$, 253 (50) $[M + H - AcOH]^+$, 193 (100) $[M + H - 2\ AcOH]^+$. − HRMS: $C_{15}H_{21}O_7$ [M + H]: calcd. 313.12873; found 313.12861.

Compound 11: Colorless oil. − R_f = 0.45 (petroleum ether/dichloromethane/diethyl ether, 2:1.5:0.5, after two successive elutions). − $[\alpha]_D^{22}$ = +87.1 (*c* = 0.88, acetone). − ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 5.84 (m, 2 H, 2-H, 2′-H), 5.39 (dd, 1 H, $J_{6,7}$ = 3.4, $J_{7,8}$ = 0.8 Hz, 7-H), 5.36 (d, 1 H, $J_{5,6}$ = 10.5 Hz, 5-H), 5.19 [m, 2 H, 1-H(*E*), 1-H(*Z*)]*, 5.18 (dd, 1 H, 6-H), 5.12 [br. d, 1 H, $J_{1(E),2}$ = 10.3 Hz, 1-H(*E*)]*, 5.08 [br. d, 1 H, $J_{1(Z),2}$ = 17.5 Hz, 1-H(*Z*)]*, 4.10 (dd, 1 H, $J_{8,9a}$ = 8.6 Hz, $J_{9a,9b}$ = 13.0 Hz, 9-Ha), 4.04 (m, 2 H, 8-H, 9-Hb), 2.72 (dd, 1 H, $J_{2',3'a}$ = 6.2 Hz, J_{gem} = 15.6 Hz, 3′-Ha), 2.45 (dd, 1 H, $J_{2,3a}$ = 6.7 Hz, J_{gem} = 14.6 Hz, 3-Ha), 2.33 (dd, 1 H, $J_{2',3'b}$ = 7.7 Hz, 3′-Hb), 2.14 (dd, 1 H, $J_{2,3b}$ = 5.8 Hz, 3-Hb), 2.16, 2.05, 2.03, 1.97 (4 s, 12 H, acetyl). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 132.3 (C-2), 131.8 (C-2′), 119.4 (C-1′), 119.2 (C-1), 78.5 (C-4), 70.2 (C-6), 69.8 (C-5), 68.4 (C-7), 68.2 (C-8), 62.5 (C-9), 41.6 (C-3), 34.0 (C-3′), 170.9, 170.8, 170.8, 169.7 (C=O), 21.3, 21.2, 21.1, 21.0 (acetyl). − *The assignments for 1′-H(*E*), 1′-H(*Z*), 1-H(*E*), and 1-H(*Z*) may be reversed. The assignments of 3-Ha, 3-Hb, 3′-Ha, and 3′-Hb were made on the basis of the assignments found for **9**. − $C_{20}H_{28}O_9$ (412.44): calcd. C 58.24, H 6.84, O 34.91; found C 58.28, H 6.84, O 33.93.

2,3,4,6-Tetra-*O*-acetylspiro[1,5-anhydro-D-glucitol-1,4′-cyclopent-1′-ene] (21): 3,3′-(D-Glucopyranosylidene)bis(1-propene) **9** (30.2 mg, 0.073 mmol) was placed in a 10-mL flask. After the flask had been flushed with argon, oxygen-free CH_2Cl_2 (3 mL) was added by syringe. Grubbs' catalyst (3.83 mg, 4.6 × 10^{-3} mmol, 6 mol %) was then added under argon. After the reaction mixture had been stirred at room temperature for 7 h, TLC monitoring showed the complete transformation of the starting material (R_f = 0.37, ethyl acetate/petroleum ether, 3:7) into a new product (R_f = 0.28, ethyl acetate/petroleum ether, 3:7), which appeared green on the TLC plate after spraying with diluted H_2SO_4 and charring. The resulting black solution was concentrated under reduced pressure. The residual dark oil was taken up in diethyl ether, stirred overnight under air to decompose the catalyst,[36] and filtered. After removal of the solvent in vacuum followed by silica gel chromatography (100 mL of ethyl acetate/petroleum ether, 3:7, then 200 mL of ethyl acetate/petroleum ether, 1:2), **21** was obtained as a white solid (22.8 mg, 81% yield). − Colorless needles (diethyl ether/petroleum ether), m.p. 106−107 °C. − $[\alpha]_D^{22}$ = +42.3 (*c* = 1, acetone). − IR (KBr): $\tilde{\nu}$ = 1750 cm^{-1} (C=O), 1725 cm^{-1} (C=C). − ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 5.63 (m, 2 H, 1′-H, 2′-H), 5.19 (m, 2 H, 2-H, 3-H), 5.09 (m, 1 H, 4-H), 4.24 (dd, 1 H, $J_{5,6a}$ = 4.4 Hz, $J_{6a,6b}$ = 12.2 Hz, 6-Ha), 4.08 (dd, 1 H, $J_{5,6b}$ = 2.4 Hz, 6-Hb), 3.83 (ddd, 1 H, 5-H), 2.85 (m, 4 H, 3′-Ha, 3′-Hb, 5′-Ha, 5′-Hb), 2.02, 2.01, 1.98, 1.96 (4 s, 12 H, acetyl). − ^{1}H NMR (500.1 MHz, $[D_6]$acetone): δ = 5.65 (m, 1 H, 1′-H), 5.64 (m, 1 H, 2′-H), 5.19 (t, 1 H, $J_{3,4}$ = 9.8 Hz, 3-H), 5.11 (d, 1 H, $J_{2,3}$ = 9.8 Hz, 2-H), 5.04 (t, 1 H, $J_{4,5}$ = 9.9 Hz, 4-H), 4.21 (dd, 1 H, $J_{5,6a}$ = 4.6 Hz, $J_{6a,6b}$ = 12.2 Hz, 6-Ha), 4.05 (dd, 1 H, $J_{5,6b}$ = 2.5 Hz, 6-Hb), 3.98 (ddd, 1 H, 5-H), 2.73 (s, 2 H, 5′-Ha, 5′-Hb), 2.52 (q, 2 H, 3′-Ha, 3′-Hb), 2.02, 2.01, 1.98, 1.96 (4 s, 12 H, acetyl). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 171.2, 170.8, 170.2, 169.9 (C=O), 128.3 (C-1′), 127.9 (C-2′), 85.4 (C-1), 73.1 (C-2), 72.8 (C-3), 70.6 (C-5), 69.2 (C-4), 62.9 (C-6), 45.6 (C-3′), 36.5 (C-5′), 21.2, 21.1, 21.0, 21.0 (acetyl). − $C_{18}H_{24}O_9$ (384.286): calcd. C 56.25, H 6.29, O 37.46; found C 56.39, H 6.37, O 37.77.

2,3,4,6-Tetra-*O*-acetylspiro[1,5-anhydro-D-mannitol-1,4′-cyclopent-1′-ene] (22): This compound was prepared from **10** (89% isolated yield) as described for **21**. Colorless oil. − $[\alpha]_D^{22}$ = +23.1 (*c* = 1.4, acetone). − ^{1}H NMR (500.1 MHz, $[D_6]$ acetone): δ = 5.68 (m, 2 H, 1′-H, 2′-H), 5.28 (d, 1 H, $J_{2,3}$ = 3.1 Hz, 2-H), 5.27 (t, 1 H, $J_{3,4}$ = 10.1, $J_{4,5}$ = 10.1 Hz, 4-H), 5.19 (dd, 1 H, 3-H), 4.18 (dd, 1 H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 12.1 Hz, 6-Ha), 4.07 (dd, 1 H, $J_{5,6b}$ = 2.6 Hz, 6-Hb), 3.97 (ddd, 1 H, 5-H), 2.86 (br. d, $J_{5'a,5'b} \approx$ 17 Hz, 5′-Ha), 2.55 (br. d, 1 H, 5′-Hb), 2.49 (br. d, 1 H, $J_{3'a,3'b} \approx$ 18 Hz, 3′-Ha), 2.43 (br. d, 1 H, 3′-Hb), 2.16, 2.04, 2.02, 1.93 (4 s, 12 H, acetyl). − ^{13}C NMR (75.5 MHz, $[D_6]$acetone): δ = 128.4 (C-1′), 127.6 (C-2′), 85.7 (C-1), 73.2 (C-2), 71.4 (C-5), 71.0 (C-3), 66.3 (C-4), 63.4 (C-6), 43.9 (C-3′), 39.0 (C-5′), 170.5, 170.3, 170.0, 169.7 (C=O), 20.3, 20.2, 20.15, 20.1 (acetyl). − $C_{18}H_{24}O_9$ (384.286): calcd. C 56.25, H 6.29, O 37.46; found C 56.19, H 6.55, O 37.16.

2,3,4,6-Tetra-*O*-acetylspiro[1,5-anhydro-D-galactitol-1,4′-cyclopent-1′-ene] (23): This compound was prepared from **11** (72% isolated yield) as described for **21**. White solid (diethyl ether/petroleum ether), m.p. 108−109 °C. − $[\alpha]_D^{22}$ = +50.7 (*c* = 0.4, CH_2Cl_2). − ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 5.56 (m, 2 H, 1′-H, 2′-H), 5.37 (d, 1 H, $J_{2,3}$ = 10.8 Hz, 2-H), 5.34 (dd, 1 H, $J_{3,4}$ = 3.3, $J_{4,5}$ = 0.9 Hz, 4-H), 4.97 (dd, 1 H, 3-H), ca. 4.0 (m, 3 H, 5-H, 6-Ha, 6-Hb), ca. 2.5 (m, 4 H, 3′-Ha, 3′-Hb, 5′-Ha, 5′-Hb), 2.10, 1.96, 1.94, 1.91 (4 s, 12 H, acetyl). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 170.4, 170.0, 170.0 (C=O), 127.9, 127.5 (C-1′, C-2′), 85.6 (C-1), 70.1 (C-3), 70.0 (C-2), 68.7 (C-5), 67.9 (C-4), 61.8 (C-6), 45.4 (C-3′), 35.9 (C-5′), 20.7, 20.7, 20.6, 20.6 (acetyl). − MS CI (isobutane) $C_{18}H_{24}O_9$ (384): *m/z* (%) = 385 (96) $[M + H]^+$, 325 (100) $[M + H - AcOH]^+$, 265 (18) $[M + H - 2\ AcOH]^+$. − HRMS calcd. for $C_{18}H_{25}O_9$ [M + H]: 385.149857, found 385.14975.

Spiro[1,5-anhydro-D-glucitol-1,4′-cyclopent-1′-ene] (24): Compound **21** (44 mg, 0.11 mmol) was dissolved in an 8:1:1 MeOH/NEt_3/H_2O mixture (6 mL). After stirring at room temperature for ca. 20 h, deacetylation was complete, as shown by TLC (R_f = 0.3, AcOEt/MeOH/H_2O, 12:5:1). Concentration under reduced pressure produced compound **24** as a colorless oil (24 mg, quantitative yield). − $[\alpha]_D^{22}$ = +39.8 (*c* = 1.27, MeOH). − ^{1}H NMR (300.1 MHz, CD_3OD): δ = 5.52 (m, 2 H, 1′-H, 2′-H), 3.66 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 11.7 Hz, 6-Ha), 3.53 (dd, 1 H, $J_{5,6b}$ = 5.2 Hz, 6-Hb), 3.32 (ddd, 1 H, $J_{4,5}$ = 9.3 Hz, 5-H), 3.25−3.18 (m, 3 H, 2-H, 3-H, 4-H), 2.66, 2.49, 2.33 (dt, dt, dd, 1 H, 1 H, 2 H, J_{gem} = 17 Hz, J_{gem} = 15 Hz, J_{gem} = 17 Hz, 3′-Ha, 3′-Hb, 5′-Ha, 5′-Hb)*. − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 129.6, 129.5 (C-1′, C-2′)*, 87.5 (C-1), 77.2, 76.4, 76.2, 72.5 (C-2, C-3, C-4, C-5)*, 63.6 (C-6), 47.0 (C-3′), 36.1 (C-5′). − *These assignments are not precisely established. − MS CI (isobutane): *m/z* (%) = 217 (47) $[M + H]^+$, 199 (44) $[M + H - H_2O]^+$, 181 (100) $[M + H - 2\,H_2O]^+$. − HRMS: $C_{10}H_{17}O_5$ [M + H]: calcd. 217.107599; found 217.10764.

Spiro[1,5-anhydro-D-mannitol-1,4′-cyclopent-1′-ene] (25): Compound **22** (48.3 mg, 0.13 mmol) was dissolved in an 8:1:1 MeOH/NEt_3/H_2O mixture (6 mL). After the mixture had been stirred for ca. 6 h at room temperature, TLC showed no traces of the starting material ($R_f \approx 0.3$, ethyl acetate/petroleum ether, 1:2), which had been converted into a polar compound (R_f = 0, ethyl acetate/petroleum ether, 1:2, and R_f = 0.66, AcOEt/EtOH/H_2O, 7:5:1). Concentration under reduced pressure provided compound **25** as an oil (29 mg, quantitative yield). − $[\alpha]_D^{22}$ = +95.4 (*c* = 1.5, MeOH). − ^{1}H NMR (300.1 MHz, CD_3OD): δ = 5.69 (m, 2 H, 1′-H, 2′-H), 3.81−3.63 (m, 5 H, 2-H, 3-H, 4-H, 6-Ha, 6-Hb), 3.41 (m, 1 H, 5-H), 2.84, 2.67, 2.48, 2.27 (4 br. d, 4 H, $J_{gem} \approx 16$ Hz, 3′-Ha, 3′-Hb, 5′-Ha, 5′-Hb)*. − ^{13}C NMR (75.5 MHz, CD_3OD): δ = 128.6, 127.4 (C-1′, C-2′)*, 86.8 (C-1), 75.5, 75.2, 72.9, 67.3 (C-2, C-3, C-4, C-5)*, 62.2 (C-6), 43.7 (C-3′), 38.5 (C-5′). − *These assignments are not precisely established. − MS EI (70 eV): *m/z* (%) = 199 (3) $[M - OH]^+$, 181 (3) $[M - H_2O - OH]^+$.

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